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(21) International Application Number: <b>PCT/EP00/00736</b> (22) International Filing Date: <b>28 January 2000 (28.01.00)</b> (30) Priority Data: 09/240,940                      29 January 1999 (29.01.99)                      US (71) Applicant (for all designated States except PL US): SAR- TOMER COMPANY, INC. [US/US]; Oaklands Corporate Center, 502 Thomas Jones Way, Exton, PA 19341 (US). (71) Applicant (for PL only): CRAY VALLEY S.A. [FR/FR]; Tour Total, 24, cours Michelet, F-92800 Puteaux (FR). (72) Inventors; and (75) Inventors/Applicants (for US only): CESKA, Gary, W. [US/US]; 310 Long Ridge, Exton, PA 19343 (US). FAN, Mingxin [CN/US]; 49 Sheffield Lane, West Chester, PA 19380 (US). HORGAN, James, P. [US/US]; 805 Copeland School Road, West Chester, PA 19380 (US). JURCZAK, Edward, A. [US/US]; 7720 Mill Road, Elkins, PA 19027 (US). MILLER, Henry, C. [US/US]; 1355 Westminster Drive, Downingtown, PA 19335 (US).		(74) Agent: CHAILLOT, Geneviève; Cabinet Chaillot, 16-20, av- enue de l'Agent Sarre, Boîte postale 74, F-92703 Colombes Cedex (FR). (81) Designated States: CA, CN, CZ, HU, JP, KR, MX, PL, SG, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.
(54) Title: <b>COMPOUNDS COMPRISING ACRYLATE AND CYCLIC SEC.-AMINE FUNCTIONALITIES</b>		
(57) Abstract <p>(Meth)acrylate functional compound which is the reaction product of a cyclic secondary amine and a multifunctional (meth)acrylate having at least three acrylate or methacrylate groups, useful for radiation curable coating or ink composition having low viscosity, low volatility, and high cure rate under radiation. Process of preparing a coating or ink composition using such compound. Radiation cured coated or ink based on such composition. Coated or printed article having such a cured coating or ink.</p>		

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## COMPOUNDS COMPRISING ACRYLATE AND CYCLIC SEC.-AMINE FUNCTIONALITIES

This invention relates to aminoacrylate monomers, process for preparation of monomers and polymers, coatings, and inks made with aminoacrylate monomers.

5           Coatings, inks, and adhesives can be prepared from (meth)acrylate monomers and oligomers by radiation curing. Radiation curing is generally done under UV or EB radiation, optionally in the presence of photoinitiators, and proceeds by a free radical mechanism. A problem in this art is that air retards or inhibits  
10 the cure, leading to tacky surfaces. German patent DE 3,706,355 suggests that amines and acrylated amines can enhance the surface cure, even in the presence of oxygen. US Patent 3,876,518 and Canadian Patent 1,011,891 teach that the modification of acrylated epoxidized soybean oil with amine at low level can enhance the surface  
15 cure which is especially useful in ink applications. Robson, et al. US Patent 4,045,416 assigned to Union Carbide Corporation teaches preparation of amine acrylates from primary and secondary amines and polyacrylates, preferably diacrylates and their use directly or as part of radiation curable formulations. Meixner, et al. US Patent  
20 5,482,649, assigned to Bayer Ak., disclosed that the modification of acrylates with primary amines at low level leads to low viscosity aminoacrylates. US Patent 3,876,518 teaches low acrylate functionality for amine acrylates in radiation cure applications.

The prior art did not teach low viscosity, low volatility,  
25 high cure rate compositions comprising multifunctional acrylates. According to the prior art, it would have been expected that modification of multifunctional acrylates with amines would lead to high viscosity or gel-like materials.

An object of the present invention was to provide reactive  
30 acrylates having low viscosity and which can be used in radiation, especially UV and EB, cure without gel formation or high viscosity.

Besides these advantages, the invention provides cured compositions containing these new acrylates with higher thermal stability, lower yellowness, lower odor and lower extractables content.

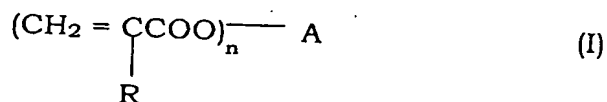
35           These objects, and others which will become apparent from the following disclosure, are achieved by the present invention which comprises in one aspect a (meth)acrylate (i.e., acrylate,

methacrylate, or mixtures thereof) functional compound which is the reaction product of a cyclic secondary amine and a multifunctional (meth)acrylate having at least three (meth)acrylate groups, useful for radiation curable coating or ink composition having low viscosity, low volatility, and high cure rate under radiation.

Other aspects of the invention include the process for preparing such coating and ink composition, the coatings and inks, articles coated with the coating or printed with the ink.

The multifunctional reactive amine acrylates of the invention can be prepared by reacting multifunctional (meth)acrylates having at least three (meth)acrylate groups with a cyclic secondary amine compound such as morpholine and/or piperidine. The reaction between acrylates and amines is known as Michael addition reaction, both primary and secondary amines are suitable.

Multifunctional acrylates are well known in the art which can be prepared from (meth)acrylic acid and tri- or tetra-hydroxy polyols in the presence of catalysts. Suitable (meth)acrylates include propoxylated glyceryl triacrylate, trimethylolpropane triacrylate, ethoxylated trimethylolpropane triacrylate, propoxylated trimethylol propane triacrylate, pentaerythritol triacrylate, tris (2-hydroxy ethyl) isocyanurate triacrylate, dipentaerythritol pentaacrylate, ditrimethylolpropane tetraacrylate, pentaerythritol tetraacrylate, ethoxylated pentaerythritol tetraacrylate, urethane acrylates, and epoxy acrylates. The general formula for acrylates are shown below :



where R is hydrogen or methyl, A is the residue of a polyol, and n is an integer having a value of 3 to 6.

The production of multifunctional (meth)acrylate esters is well known to those of normal skill in the art. It is known that an acid such as acrylic acid or methacrylic acid will react with a polyhydroxyl compound to produce the multifunctional (meth)acrylate ester. The multifunctional (meth)acrylate esters can also be produced by transesterification reactions. These reactions are known in the art and

the conditions under which they are carried out are so well known that they need not be set forth in detail.

The polyols that are reacted with acrylic acid or methacrylic acid to produce the multifunctional (meth)acrylate esters can be any of the compounds containing three or more hydroxyl groups that will undergo esterification. These are well known and include the aliphatic-type polyols having from three to about 20 carbon atoms, triols such as trimethylol propane, glycerol, 1,2,6-hexanetriol ; tetrols such as pentaerythritol ; and the like ; the ether polyols having a molecular weight of from about 106 to about 15,000, including the block polyoxyalkylene polyols.

Hence, the residue of the polyol used to produce the multifunctional (meth)acrylate ester can be a saturated or unsaturated linear or branched polyvalent alkylene.

Suitable secondary cyclic amines include morpholine, substituted morpholines, piperidine, substituted piperidines, and the like. The preferred amines are morpholine and piperidine. The morpholine or piperidine can be modified, for example the reaction product of piperazine or alkyl substituted piperazines with mono-epoxides such as epichlorohydrin, styrene oxide, ethylene oxide, propylene oxide, butylene oxide, cyclohexane oxide, and the like, or poly-epoxides such as diglycidyl ether of bisphenol A, 4-vinyl-1-cyclohexene dioxide, and the like ; the reaction product of said piperazines with an isocyanate such as phenyl isocyanate, methyl isocyanate, tolylene diisocyanate, bis(2-isocyanatoethyl)bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylate, bis(2-isocyanatoethyl)4-cyclohexene-1,2-dicarboxylate, and the like. In these instances only one of the >NH groups of the piperazine compound is reacted and there is always an >NH group available from the piperazine molecule.

The reaction between the acrylates and secondary cyclic amine can take place without any catalyst or solvent. The reaction can be carried out at temperature between -30 to 150°C, the preferred temperature is from 25 to 100°C. Although solvent is not required, it may be used to facilitate the heat and mass transfer. The reaction of the multifunctional (meth)acrylate ester with the amine is preferably carried out in an inert gas atmosphere, for example, under nitrogen or argon, to prevent or minimize unwanted side reactions. However, this

is not necessary for a successful reaction. The reaction can be carried out at a temperature of from  $-30^{\circ}\text{C}$  or lower to about  $150^{\circ}\text{C}$  or higher. The preferred temperature range is from about  $-10^{\circ}\text{C}$  to about  $75^{\circ}\text{C}$ , and the most preferred range is from about  $15^{\circ}\text{C}$  to about  $60^{\circ}\text{C}$ . The pressure of the reaction system can be maintained at atmospheric pressure or superatmospheric pressure.

To prevent acrylate polymerization, various inhibitors or stabilizers may also be used during the reaction. Typical inhibitors such as hydroquinone, hydroquinone methyl ether, butylated hydroquinone can be used.

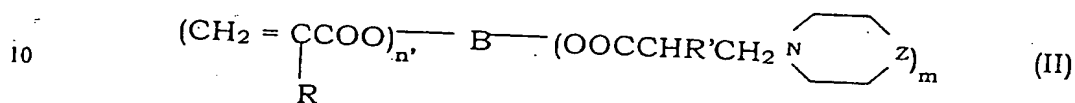
Solvent may be used to facilitate heat and mass transfer during the reaction which was exothermic. Non-reactive solvents such as hydrocarbons, esters and halogenated solvents may be used. Examples are toluene, hexane, heptane, ethyl acetate, butyl acetate, chloroform, chlorobenzene. The reaction can be carried out in the absence of a solvent or in the presence of an inert solvent. Among the suitable inert organic solvents that can be used one can mention methanol, ethanol, acetone, benzene, toluene, xylene, hexane, octane, and the like. Any inert solvent can be used that does not interfere with the reaction. In order to minimize side reactions, the reaction is preferably carried out in the absence of light.

In the reaction, one or more of the acrylyl groups of the multifunctional (meth)acrylate ester reacts to displace the amino hydrogen atom while the rest of acrylyl group of the multifunctional (meth)acrylate ester is not affected. The molar amount of amines charged to the reaction system can vary from about 0.9 mole to about 3 moles or more per mole of multifunctional (meth)acrylates to produce the oligomers.

In carrying out the reaction, the polyacrylate ester can be added to the amino compound or the amino compound can be added to the multifunctional (meth)acrylate ester ; the latter procedure is preferred. At the completion of the reaction, the amine acrylates are recovered as residue products ; however, in some instances recovery by conventional distillation and fractionation procedures is possible. The amine acrylates can also be prepared by simultaneously spraying separate streams of the amine compound and the multifunctional (meth)acrylate ester onto a surface or into an enclosed area. In many

instances, the reaction is rapid and the two components quickly co-react. The means for simultaneously feeding two or more separate streams in the proper ratios are known in the art and such equipment does not constitute a part of this invention.

5 The final products have both acrylate and amine functionality with the following general structure :



where R is hydrogen or methyl, B is the residue of a polyol, R' is hydrogen or methyl, Z is oxygen, CH<sub>2</sub>, or nitrogen containing group, n' is an integer of 1 to 6, and m is an integer of 1 to 5, and when n' is higher than 1, the R are identical or different, and when m is higher than 1, the R' are identical or different.

These acrylates were found to be very effective synergists in UV/EB curing and can be used alone or along with other acrylate monomers and oligomers. In the present invention, the aminopolyacrylates were evaluated as part of the formulation vs some commercial products. The results showed that these new polymerizable synergists are very effective and higher activity was observed. As previously indicated, the amine acrylates are readily cured by ultraviolet light radiation or electron beam radiation or high intensity predominantly continuum light radiation. The curing is very rapid and a durable protective film is formed.

The coating compositions can be applied to a surface by any of the known conventional means, including the spray, curtain, dip, pad and roll-coating techniques. The substrate to be coated can be any composition ; for example, wood, metal, paper, plastic, fabric, fiber, ceramic, concrete, plaster, glass, etc.

The amine acrylate-containing compositions can be cured by ionizing radiation, either particulate or non-particulate, or non-ionizing radiation. As a suitable source of particulate radiation, one can use any source which emits electrons or charged nuclei.

The use of low to high pressure mercury lamps to generate ultraviolet light is known. The cure time depends on the light intensity and the specific formulation. An appreciable period of time is generally needed for completion of a reaction when a material is exposed to the low intensity ultraviolet radiation generated from a mercury lamp.

The rate of curing can be enhanced by the addition of suitable photosensitizers and photoinitiators. Illustrative of suitable photosensitizer compounds one can mention acetophenone, propiophenone, benzophenone, xanthone, fluorenone, benzaldehyde, fluorene, anthraquinone, triphenylamine, carbazole, 3- or 4-methylacetophenone, 3- or 4-pentylacetophenone, 3- or 4-methylbenzophenone, 3- or 4-chlorobenzophenone, 4,4'-bis(dimethylamino)benzophenone, 4,4'-dimethoxybenzophenone, 4-chloro-4'-benzylphenone, 3-chloroxanthone, 3,9-dichloroxanthone, 3-chloro-8-nonylxanthone, 3-methoxyxanthone, 3-iodo-7-methoxyxanthone, and the like. As is obvious one can use a mixture of photosensitizers. Examples of photoinitiators are 1-hydroxycyclohexyl phenyl ketone, 2-benzyl-2-N, N-dimethylamino-1-(4-morpholinophenyl)-1-butanone, 1-hydroxycyclohexyl phenyl ketone, 2,2-dimethoxy-2-phenyl acetophenone, and 2-hydroxy-2-methyl-1-phenyl-propan-1-one. The amount of photosensitizer or photoinitiator used can vary from about 0.01 to about 20 weight per cent of the coating solution. A preferred amount is from about 0.1 to about 5 weight per cent, and most preferred is a concentration of from about 0.5 to about 3 weight per cent. A mixture of photosensitizer and/or photoinitiators can also be used.

As previously indicated, the amine acrylates, singly or in mixtures, can be blended with from 1 to about 50 weight per cent or more of other coating compositions that are known to cure on exposure to radiation. The concentration of amine acrylates blended in such compositions can vary from about 1 to 99.9 weight per cent of the coating composition, preferably from about 10 to about 75 weight per cent. These coating compositions can also contain from about 5 to about 50 weight per cent of a polymerizable solvent such as styrene or a high boiling acrylyl ester.

The coating compositions are produced by mixing the selected components thereof by conventional known methods. The blend can be heated, if desired, to facilitate mixing.



Coating compositions having the amine acrylate compound present, alone or in admixture, can contain fillers, pigments and other additives conventionally present in coating compositions. These additives are so well known to those skilled in the art that they need no specific mention ; nor it is necessary for an understanding of this invention to recite concentrations thereof. The same can be said of the known radiation curable coating compositions that can be admixed with the amine acrylates to improve the curing and crosslinking properties.

### Examples

The following non-limiting examples are presented to illustrate a few embodiments of the invention. All parts and percentages are by weight unless otherwise indicated.

Procedure for UV cure formulation :

Coating formulations : all components were weighed into amber glass jars and heated in a 60°C forced-air oven before mixing on a electric stirrer at moderate speed.

Substrate : Leneta form 2A.

Application : the coatings were cured using one 23,6 kwatt/m (600 watt/inch) Fusion H lamp at full power in air at the lamp height at 15,2 m/min (50 fpm) line speed. The line speed was varied for the surface cure measurements.

Surface cure speed : the surface cure speed was determined by using both a wooden tongue depressor and the back of a fingernail. The tongue depressor was lightly scratch across the surface of the coating using its edge. Moderate pressure was also used in the fingernail scratch test. Both tests gave the same results. The fastest line speed (in 10 fpm or 3,05 m/min increments, in the 40-1000 fpm or 12,2-304,8 m/min range) was reported where no mark was apparent on the coated surface.

MEK double rubs : MEK double rubs were determined using panels that were cured at 15,2 m/min (50 fpm). The test was run over the black section of the Leneta chart using moderate pressure.

5           Example 1

Ethoxylated trimethylolpropane triacrylate (Sartomer SR 454, 428.0 grams) was reacted with morpholine (87.0 grams). The reaction was kept at 50°C for 4 hours which resulted in a clear, light  
10   yellow liquid.

Example 2

Example 1 was repeated with 428.0 g of propoxylated  
15   glycerol triacrylate (Sartomer SR 9020) instead of ethoxylated trimethylolpropane triacrylate.

Example 3

20           Example 1 was repeated with trimethylolpropane triacrylate instead of ethoxylated trimethylolpropane triacrylate.

Example 4

25           In a reactor, 300.0 g of tripropylene glycol triacrylate was placed and air sparge was applied. Morpholine (136.8 g) was added slowly under stirring, exothermic reaction took place as indicated by temperature increase. The reaction was kept at 50°C for 4 hours. A clear, light yellow liquid was obtained.

30

Example 5

In a reactor, 296.0 g of trimethylolpropane triacrylate was placed and air sparge was applied. Morpholine (174.0 g) was added  
35   slowly under stirring, exothermic reaction took place as indicated by temperature increase. The reaction was kept at 50°C for 4 hours. A

## UV cure study

Product	CN120 EA (g)	SR351 TMPTA (g)	SR306 TPGDA (g)	Crystalline Benzophe- none (g)	Amine synergist (g)	MSCS (m/min)	MEK double rub
Blank (no amine)	34	26	33	5	0	3	10
MDEA	34	26	33	5	4.7	30.5	200
Ebecryl P104	34	26	33	5	4.7	21.3	200
Ebecryl P115	34	26	33	5	4.7	15.2	200
Ebecryl 7100	34	26	33	5	4.7	18.3	200
E4	34	26	33	5	4.7	33.5	200
E5	34	26	33	5	4.7	30.5	200
E6	34	26	33	5	4.7	30.5	200
E7	34	26	33	5	4.7	27.4	200
MDEA	34	26	33	5	9.30	36.6	200
Ebecryl P104	34	26	33	5	9.30	33.5	200
Ebecryl P115	34	26	33	5	9.30	48.8	200
Ebecryl 7100	34	26	33	5	9.30	21.3	200
E4	34	26	33	5	9.30	54.9	200
E5	34	26	33	5	9.30	61	200
E6	34	26	33	5	9.30	54.9	200
E7	34	26	33	5	9.30	51.8	200
MDEA	34	26	33	5	13.9	33.5	160
Ebecryl P104	34	26	33	5	13.9	27.4	200
Ebecryl P115	34	26	33	5	13.9	12.2	200
Ebecryl 7100	34	26	33	5	13.9	21.3	200
E4	34	26	33	5	13.9	48.8	200
E5	34	26	33	5	13.9	48.8	200
E6	34	26	33	5	13.9	48.8	132
E7	34	26	33	5	13.9	48.8	100

clear, light yellow liquid was obtained with 2.5 Pa.s (2500 cps) viscosity at 25°C.

#### Example 6

5

In a reactor, 428.0 g of ethoxylated trimethylolpropane triacrylate (Sartomer SR 454) was placed and air sparge was applied. Morpholine (174.0 g) was added slowly under stirring, exothermic reaction took place as indicated by temperature increase. The reaction  
10 was kept at 50°C for 4 hours. A clear, light yellow liquid was obtained with viscosity of 2.7 Pa.s (2700 cps) at 25°C.

#### Example 7

15

In a reactor, 450.0 g of propoxylated glycerol triacrylate (Sartomer SR 9021) was placed and air sparge was applied. Morpholine (136.6 g) was added slowly under stirring, exothermic reaction took place as indicated by temperature increase. The reaction  
20 was kept at 50°C for 4 hours. A clear, light yellow liquid was obtained with viscosity of 2.65 Pa.s (2650 cps) at 25°C.

#### Example 8 – UV cure study of various aminoacrylates

Some of the products from the above samples were tested  
25 in the specified formulations at three different levels and both surface cure and MEK double rubs (solvent resistance) were measured.

- 11 -

CN 120 is an epoxy acrylate from Sartomer Company, Inc.

SR 351 is trimethylolpropane triacrylate from Sartomer.

SR 306 is tripropylene glycol diacrylate from Sartomer.

MSCS – maximum surface cure speed.

5 MEK – MEK double rubs for testing solvent resistance.

MDEA is methyl diethanol amine.

Ebecryl P104 and Ebecryl P115 are amine synergists based on diacrylates and secondary amines marketed by UCB Radcure.

10 Ebecryl 7100 is an amine synergist based on diacrylate and primary amine marketed by UCB Radcure.

E4, E5, E6 and E7 are materials prepared from examples 4, 5, 6 and 7 respectively.

15 Thermal stability of the cured films

Formulations in the above example with 15% amine synergists (third level of content in table of example 8) were cured and the cured polymer films were analyzed by TGA to determine the  
20 thermal stability of the cured polymers. The formulations with the synergists E5, E6, E7 based on the invention showed much better thermal stability of the cured polymers, as shown on figure 1 presenting the thermal stability of the cured polymers (% of weight as a function of temperature). The amine synergist content for the cured  
25 polymers of figure 1 is 15% by weight with respect to the total weight of the other reactive components.

While the invention has been described and exemplified in detail, various alternative embodiments should become apparent to  
30 those skilled in the art without departing from the spirit and scope of the invention.

CLAIMS

1 - (Meth)acrylate functional compound which is the reaction product of a cyclic secondary amine and a multifunctional (meth)acrylate having at least three acrylate or methacrylate groups, useful for radiation curable coating or ink composition having low viscosity, low volatility, and high cure rate under radiation.

2 - Compound according to claim 1 wherein the multifunctional (meth)acrylate is selected from the group consisting of triacrylates, tetraacrylates, pentaacrylates, and hexaacrylates.

3 - Compound according to claim 1 or 2 wherein the cyclic secondary amine is selected from the group consisting of morpholine and piperidine.

4 - Compound according to claim 3, wherein the cyclic amine is morpholine.

5 - Process of preparing coating and ink compositions comprising curing a composition comprising a compound according to anyone of claims 1 to 4 in the presence of radiation.

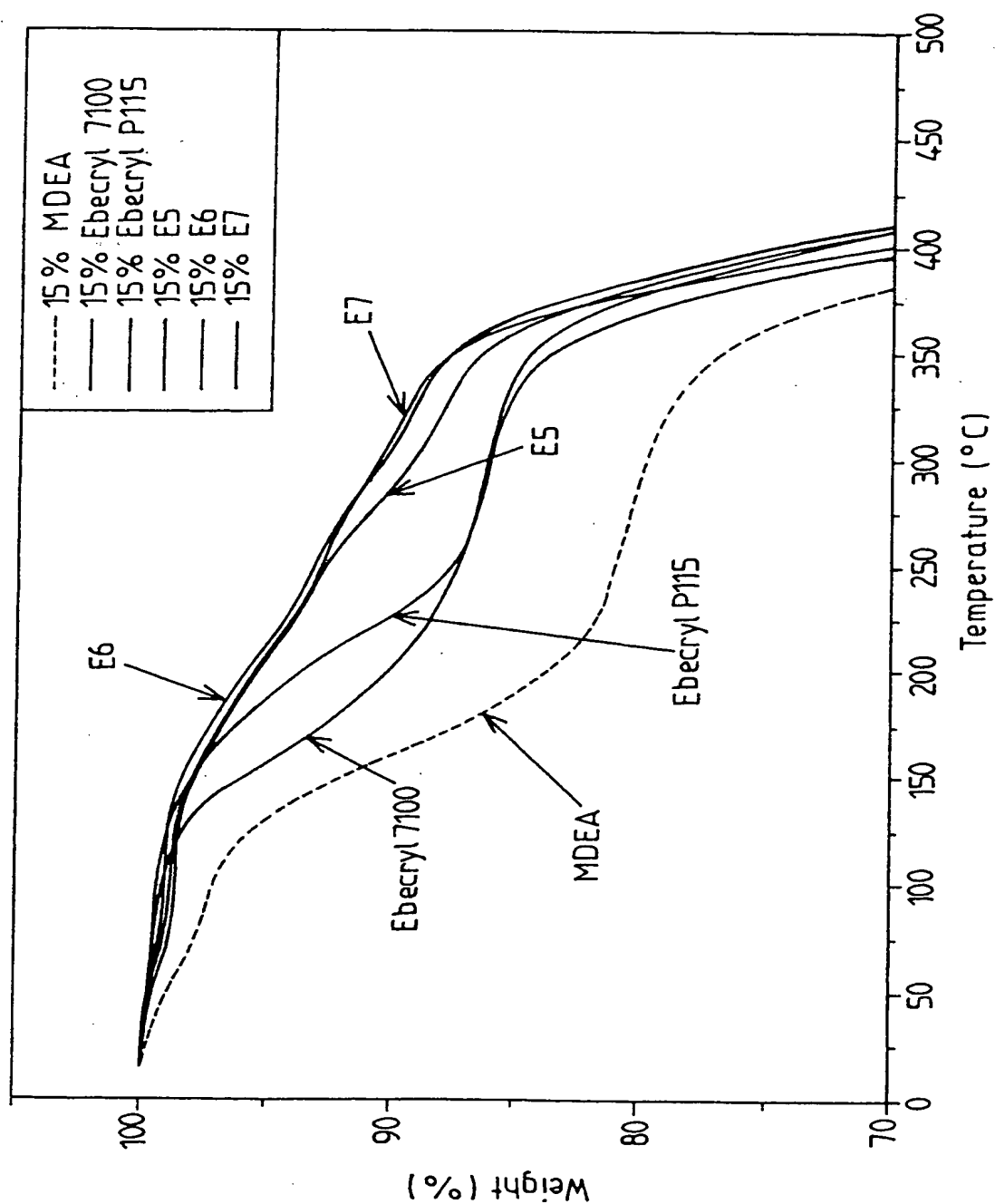
6 - Composition useful for radiation cured coatings and inks comprising a compound according to anyone of claims 1 to 4 and one or more other acrylate compounds, said composition having low viscosity, low volatility, and exhibiting a high cure rate.

7 - Composition of claim 6, further including a polymerization initiator.

8 - Coating or ink cured from a composition of claims 6 or 7 in the presence of radiation.

9 - Coated or printed article having a cured coating or ink of claim 8.

FIG. 1



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/00736

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 7 C07D295/108 C09D4/00 C09D11/10

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)  
IPC 7 C07D C09D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 974 131 A (PUSKAS JOSEPH EMIL ET AL) 10 August 1976 (1976-08-10) column 3 -column 5; examples 1-4	1,2
X	PATENT ABSTRACTS OF JAPAN vol. 018, no. 528 (C-1258), 6 October 1994 (1994-10-06) & JP 06 184473 A (DAINIPPON TORYO CO LTD;OTHERS: 01), 5 July 1994 (1994-07-05) abstract	1,2
A	US 5 596 669 A (NOREN GERRY K ET AL) 21 January 1997 (1997-01-21)	1,2
A	US 4 045 416 A (ROBSON JOHN HOWARD ET AL) 30 August 1977 (1977-08-30) cited in the application	1-3,5
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/EP 00/00736

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
L	<p>DATABASE CHEMABS 'Online! CHEMICAL ABSTRACTS SERVICE, COLUMBUS, OHIO, US SHIONO, TERUO ET AL: "Active energy beam-curable compositions with excellent curability in oxygen, the cured film formation, and the cured products thereof" retrieved from STN Database accession no. 132:266534 XP002137622 abstract</p>	1-9
E	<p>&amp; JP 2000 109522 A (TOYO INK MFG. CO., LTD., JAPAN) 18 April 2000 (2000-04-18)</p>	1-9

# INTERNATIONAL SEARCH REPORT

Information on patent family members

Int. J. Appl. No.

PCT/EP 00/00736

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3974131 A	10-08-1976	NONE	
JP 06184473 A	05-07-1994	NONE	
US 5596669 A	21-01-1997	NONE	
US 4045416 A	30-08-1977	US 3963771 A	15-06-1976
JP 2000109522 A		NONE	